

PATENT SPECIFICATION

(11) 1448320

1 448 320

- (21) Application No. 50972/74 (22) Filed 25 Nov. 1974
(31) Convention Application No. 447 883
(32) Filed 4 March 1974 in
(33) United States of America (US)
(44) Complete Specification published 2 Sept. 1976
(51) INT CL² C04B 43/00
(52) Index at acceptance
C3N 25 25A3 25C2 25G2 25G3 25G4 25G6 25GX 25K1A
25K1B2 25K1Y

C1k 18
1740nt



(54) LIGHTWEIGHT INORGANIC MATERIAL

(71) We, WASHINGTON STATE UNIVERSITY RESEARCH FOUNDATION, INC., a Corporation organised and existing under the laws of the State of Washington, United States of America, of Pullman, State of Washington, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a lightweight inorganic material containing fly ash cenospheres, phosphoric acid and optionally metal phosphates. The phosphoric acid and metal phosphates are initially contained in a liquid binder solution. When mixed with fly ash cenospheres and after heating of the mixed mass to a temperature below the sintering temperature of the cenospheres, a rigid, lightweight inorganic material is produced which has particular value as a construction insulating material.

Modern utilization of rigid plastic foams as insulating materials in building and construction presents serious hazard in case of fire. Fire tests in the laboratory, particularly with respect to plastic materials, are inaccurate and tell little about how a material will perform in a real building fire. The fact that a plastic material is not flammable has lulled the consumer into a false sense of security. The toxicity of the fumes developed by plastics in a building fire forms an additional hazard. These uncertainties and the potential danger of unrestricted use of plastics, particularly foamed plastics in building and construction, have been recently publicly denounced. The quick spread of recent building fires has frequently been blamed on the use of plastic as a component of walls or partitions.

While the plastics industry is aware of this flammability crisis and the danger of plastics in the case of fire, its attempts to counter the problem have been mainly directed to the incorporation of increasing amounts of

fire-retardant chemicals into plastics. One industry source predicts that close to nine billion pounds of plastics would consume over one billion pounds of fire-retardant chemicals by 1980. However, toxic fumes evolved from these fire-retardant chemicals will only be added to those resulting from the plastics themselves when decomposing under heat. Even strongly "fireproofed" plastics will eventually become ignited, adding to the conflagration and flame spread by burning drippings. It may well be that the plastic industry is fighting a losing battle and that no "safe" plastic foam will ever be developed at a reasonable cost for building purposes.

This situation is particularly serious in the case of rigid plastic foams when used as wall or door insulation materials or as ceiling tiles in homes or in vehicles. In these cases, an inorganic and non-flammable lightweight material ought to be used instead. This need for a rigid, lightweight inorganic insulating material led to the development of the method and composition of matter described and claimed below.

This disclosure is concerned with material made of fly ash cenospheres separated from fly ash, and other additives, held together by an inorganic, heat-stable cement.

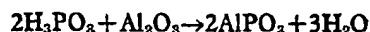
Cenospheres are hollow microspheres found in fly ash, the ash formed when pulverized coal is burned. Large quantities of cenospheres are produced as a waste product at coal-fired electricity generating stations. The fly ash is disposed of at such stations by mixing it into a slurry with water and pumping the slurry into a manmade lagoon or pond. The cenospheres then float to the surface and may be readily collected. Such ponds are found in many parts of the world.

The quantity of cenospheres in fly ash varies from less than 0.01 to 4.8 percent by weight, but by volume the quantity of cenospheres can reach as much as 20%. They have a density of about 0.6 g/cm^3 . Fillite Ltd. in England has developed a separation process which results in commercial quantities of cen-

City of
interest



- pheres having a density of 0.4 gm/cm³. Chemically, cenospheres consist essentially of the following components by weight SiO₂ (55—61%) and Al₂O₃ (26—30%), with smaller quantities of Fe₂O₃ (2—10%), CaO (0.2—0.6%), MgO (1—4%), and Na₂O, K₂O (0.5—4.0%). By their high content of Al₂O₃, they differ distinctly in composition from commercial glass microspheres.
- 10 Prior researchers have studied the behaviour of syntactic foams comprising epoxy resin-bonded cenosphere structure under hydrostatic pressure. This material was proposed for use as a buoyancy material in deep submersible vehicles. Some preliminary pressurization experiments on these syntactic foams were carried out and suggested that cenospheres will probably perform as well as the manufactured microspheres for at least some applications.
- 15 Although epoxy resin-bonded cenospheres had yielded structures which combined low density (0.4 to .83 g/cm³) with high compressive strength, they contained three parts by weight of the epoxy resin for two parts by weight of the cenospheres. When subjected to intense heat, composites with such high resin contents will still give up toxic fumes and are likely to disintegrate.
- 20 In search for an inorganic cement to re-
- place the organic polymer, we found that phosphoric acid would serve as this binder when mixed with cenospheres. After gradual heating of these premolds the mixed mass yields lightweight, rigid inorganic specimens of good structural integrity.
- 25 It is believed that the cementing of the cenospheres is effected by formation of chemical bonds between the phosphoric acid and the aluminum oxide in the cenospheres under elimination of water molecules, *viz.*,



This scheme is substantiated by the fact that only natural cenospheres, but no synthetic microballoons, can be effectively welded together by phosphoric acid, since the synthetic microballoons do not contain Al₂O₃ in their chemical composition.

In preliminary tests, structure with a density as low as 0.24/cm³ could be made with cenospheres produced by Fillite Ltd., England, and with a density of 0.48g/cm³ with water-floated cenospheres from West Virginia, U.S.A. Data on compressive strength of a few samples, together with the temperatures to which they had been heated, are shown in the following table:

SAMPLE	PREPARED AT °C	DENSITY g/cm ³	COMBINED STRENGTH Kg/cm ²
Fillite Cenospheres	200	.40	41
Fillite Cenospheres	950	.37	23
Cenospheres from West Virginia, Water-floated	200	.49	29
Cenospheres from West Virginia, Water-floated	950	.48	17
Cenospheres from West Virginia, Untreated	200	.72	64
Cenospheres from West Virginia, Untreated	950	.66	31

- According to the present invention there is provided an inorganic composition that forms a rigid monolithic lightweight mass upon application of external heat; said composition comprising cenospheres separated from the fly ash formed when pulverized coal is burned, and phosphoric acid.
- 60 The composition may also comprise a source of metal ions. As discussed below, where hygroscopic properties are no problem,
- 65 cenospheres and phosphoric acid alone may be used to produce the composition.
- The present invention also provides an inorganic composition that forms a rigid monolithic lightweight mass upon application of heat, said composition consisting essentially of a liquid binder comprising phosphoric acid, a source of metal ions and sufficient water to form a solution of metal phosphate and free phosphoric acid, and cenospheres separ-

ated from fly ash formed when pulverized coal is burned.

The metal ions produce metal phosphate in the binder liquid. Metal phosphate can be produced *in situ* during the preparation of the binder liquid or can be obtained from conventional sources of commercial metal phosphates.

In a further aspect the present invention also provides a method of bonding cenospheres to produce a rigid, lightweight material, comprising the steps of mixing spheres separated from fly ash with a liquid binder containing phosphoric acid to produce a moldable paste; molding the paste into a mass having a desired physical configuration; and heating the molded mass to a temperature below that temperature at which sintering of the cenospheres occurs.

In practice the present invention provides a lightweight inorganic material that is fire-proof and which shows considerable promise as an insulating material for building and construction purposes. The composition of the present invention is commercially desirable utilizing cenospheres produced as a waste by-product in coal-fired electrical generating plants and similar installations.

It has been known for years that a small proportion of the particles in pulverized-coal ash consists of thin-walled hollow spheres commonly termed "cenospheres". The apparent density of these fly ash cenospheres is less than that of water. They separate from the dense ash in settlement lagoons. Different amounts of the lightweight cenospheres are produced by the boilers at different power stations. In some cases the quantity of ash cenospheres is negligible. Other boilers discharge sufficient amounts of cenospheres to form a thick layer of floating material on lagoons. The amount of cenospheres is influenced by the nature of the mineral matter in the coal being fired and the method of fly ash selection and disposal.

The following constitutes a brief summary of the properties of cenospheres:

- a. Cenospheres average 20 to 200 microns in diameter and are regular spheres with coherent, non-porous shells of silicate glass. The thickness of shell is about 10% of the radius. The true particle density of the individual spheres is in the range of 0.4 to 0.6 g/cc and the bulk density 0.25 to 0.40 g/cc.
- b. The floating spheres collected from lagoons are free from soluble matter.
- c. The hollow spheres start to sinter at 1200°C. and collapse above 1300°C.
- d. The gas in the cenospheres consists mainly of CO₂ and H₂. At room temperature, the internal pressure is 0.2 atmos.
- e. The cenospheres are formed at an estimated temperature of 1400°C. and the formation and size are governed by the

viscosity and surface tension of the fused silicate glass, by rate of change in particle temperature and the rate of diffusion of gases in the silicate. The molten spheres freeze at 1000°C. trapping the gases which are formed internally through the catalytic action of ferric oxide or carbonaceous material present.

f. The chemical composition of cenospheres is somewhat variable but the principal constituents are aluminum, silicon and oxygen. The range of chemical composition (percent) by weight as follows:

Silica (as SiO ₂)	55 to 61
Alumina (as Al ₂ O ₃)	26 to 30
Iron Oxides (as Fe ₂ O ₃)	2.0 to 10
Calcium (as CaO)	0.2 to 0.6
Magnesium (as MgO)	1.0 to 4.0
Alkalies (as Na ₂ O, K ₂ O)	0.5 to 4.0
Loss on ignition	0.01 to 2.0

It is obvious from the foregoing composition that a cenosphere is a glassy matrix of calcined clay in which the gases have had no opportunity to escape.

Some generating plants discharge sufficient quantities of fly ash cenospheres to form a thick layer of floating material on lagoons. The floaters may create a significant air pollution problem, since on a warm day the top surface can dry and be blown away. Given favorable raw material and environmental conditions during combustion, one can expect as much as 4 to 5% by weight, or, on a volume bases, as much as 15 to 20% of the fly ash to consist of cenospheres.

In comparison to the dense fly ash material, the silica content of the cenospheres is higher, but the calcium oxide content is lower. Cenospheres also contain a small amount (0 to 2% by weight) of soluble material, in contrast with two to five percent by weight of soluble material in precipitated fly ash.

Observations under optical and electron microscopes have shown that fly ash cenospheres are colorless glass spheres of sizes ranging from 20 to 200 microns. There is a noticeable absence of small particles, less than 10 microns in diameter, commonly found in dense fly ash, excluding the usual small amount of debris from broken spheres. The cenospheres do have a demonstrated absence of pores on their surfaces. Blisters are occasionally seen on large particles.

The separation of dried cenospheres into different size fractions by sieving is much easier than with precipitated fly ash. The absence of the sub-micron particles prevents the formation of agglomerates and clogging of sieves. Cenospheres are much larger than the particles of dense precipitated fly ash from a given station. For example, floating ceno-

- 5 spheres contain only five percent by weight of particles that are less than 50 microns in diameter, wherein dense precipitated fly ash might have more than 80% below this size.
- 10 The behaviour of cenospheres at high temperatures has been observed by heating in a microscope. Published reports state that no change in size or in shape of the cenosphere occurs up to approximately 1250°C. Above this temperature the size of the particles slowly decrease, and at 1300°C. they collapsed to a dense blob. Cenospheres from several sources were tested and it was found that they all collapsed at approximately the same temperature.
- 15 The collapse without expansion or sudden gas release suggests that either there was a partial vacuum in the particles or that the diffusion of gas in the particle shell was sufficiently rapid to prevent increase of internal pressure on heating. A rapid collapse of particles took place when these were inserted in a furnace at 1400°C.
- 20 On sintering there has been observed a marked difference in cenospheres in comparison with dense precipitated fly ash. Pellets made of cenospheres require heating to 1200°C. before a bond by sintering occurs.
- 25 Dense precipitated fly ash starts to sinter at 1000°C. to 1100°C. and there is no significant change of volume during sintering. The high sintering temperature of fly ash cenospheres is probably due to the absence of sub-micron particles, and perhaps also to the fact that some of the low melting glass is dissolved during separation of cenospheres from the dense ash by flotation in water.
- 30 Another possible explanation is that the stable cenospheres form only from the silicates of a higher softening temperature.
- 35 These cenospheres are the starting material for a lightweight and fireproof material which is capable of replacing plastic foam in many applications, particularly as an insulating material for building and construction purposes. Tests of this material have shown it to be stable at temperatures as high as 2000°F.
- 40 It will simply not burn because of its totally inorganic nature. Furthermore, the material can be produced inexpensively from the waste by-product cenospheres. The material is believed to be an economic substitute for plastic in the manufacture of ceiling and wall tiles, door cores, insulation, trims and molding.
- 45 We have found that we can bond cenospheres with phosphoric acid plus various metal phosphates. The ones tested and shown to be satisfactory are aluminum, zinc, magnesium and chromium. Other metal phosphates are also satisfactory. The cenospheres can be bonded by using only phosphoric acid but this produces a very hygroscopic product. The metal phosphates seem to prevent this hygroscopicity.

The optimum amount of the acid-phosphate mix appears to be in the range of 1 part by weight acid mix to 0.5 to 3.5 parts of cenospheres. The acid-phosphate mix composition depends upon the individual metal phosphate as some of them are not very soluble in phosphoric acid. In all cases, the metal phosphates have been made *in situ* by adding a suitable oxide, hydroxide or carbonate to the acid. There is no reason however, to preclude the use of commercial metal phosphates if they are available. The range of molar ratios of metal phosphates to free phosphoric acid is from 0.1/1 to 1/1.

The times and temperatures of curing the premolds of binder and cenospheres can be varied from 3 hours at 500°C. to 48 hours at 600°C. and even to 3 hours at 700°C. but the optimum time and temperature seems to lie between 8 and 24 hours at 600°C. Heating the premolds to temperatures in the range 200 to 950°C. yields specimens of great structural integrity. Compressive strengths generally are about 750—800 pounds per square inch but values up to 1500 psi have been obtained.

Example 1.

The binder liquid was prepared by adding Al(OH)_3 and H_2O to 85% by weight H_3PO_4 with heating to cause solution.

	Grams
H_3PO_4 (85% by weight)	384
Al(OH)_3	78
H_2O	138

Thirty grams of the above binder solution was added to 90 grams of cenospheres. After careful mixing, the material was pressed into a mold, removed from the mold, and dried overnight at 80°—90°C. The dried, molded material was then heated to 60°C. for 8 hours and then cooled slowly.

Example 2.

A binder liquid of the following composition was prepared:

H_3PO_4 (85%)	354 Grams	110
Zn(OH)_2	185 Grams	
H_2O	126 Grams	

The cenospheres were mixed with the binder liquid in the ratio of 3 parts by weight of cenospheres to 1 part by weight of binder liquid. The material was molded and dried as in Example 1. It was then heated for curing to 60°C. for 24 hours.

Example 3.

Binder Liquid	Grams	120
H_3PO_4 (85%)	317	
MgO	30	
H_2O	52	

The cenospheres and binder were mixed in the weight ratio of 3:1, molded and cured as in Example 1.

Example 4.

5	Binder Liquid	Grams
	H ₃ PO ₄ (85%)	384
	Al (OH) ₃	78
	Mg ₃ (PO ₄) ₂ · 5H ₂ O	30
	H ₂ O	138

10 The cenospheres and binder were mixed in the weight ratio of 3:1, molded, dried and cured as in Example 1.

15 The formulations can be adjusted so that the cured material is not hygroscopic, i.e., it will absorb less than 0.5 percent of its weight of water when kept at 100% relative humidity for 12 weeks. All formulations, however, absorb water readily when immersed. They can be waterproofed by surface treatment with silane or other compounds of the type used to waterproof brick and concrete.

20 It is possible to accurately control the density of the lightweight resulting material. Density can be controlled by choice of the cenospheres. Cenospheres vary in density and size from one source to another, and can be effectively segregated by size, using known sieve procedures. One can also blend cenospheres of various sizes to develop the required density in the final product.

25 The addition of a foaming agent in the acid also tends to produce porosity in the final product. The metal carbonates previously discussed as a source of metal ions are an example of such a foaming agent. Metal powders, such as aluminum and magnesium can also be used as a foaming agent. It is also possible to use an organic filler in the composition which volatilizes when heated. Examples would be hollow phenolic beads or solid polystyrene or polyethylene powders. To make a heavier material, available fly ash can be utilized as a filler, although obviously other inorganic fillers can be added as desired.

30 The method of bonding the cenospheres comprises the mixing of cenospheres with a liquid binder containing phosphoric acid. The binder and cenospheres are mixed to produce a moldable paste. The paste is then molded into a mass that has the desired physical configuration in the product being produced. The premold is preferably allowed to dry. Overnight drying is normally sufficient when using compositions as discussed in detail above. Finally, the molded mass is heated to an elevated curing temperature below that at which sintering of the cenospheres occurs. Sintering is undesirable because of the notable loss of volume that results.

35 The liquid binder should preferably include a source of metal ions. Suitable sources of metal ions for *in situ* production of metal

phosphate are metal oxides, hydroxides or carbonates. The liquid binder may be in the form of a solution of metal phosphate, free phosphoric acid and sufficient water to form a solution of metal phosphate and free phosphoric acid. The solution is preferably a saturated solution of the metal phosphate in phosphoric acid.

65

70

WHAT WE CLAIM IS:—

1. A method of bonding cenospheres to produce a rigid, lightweight material, comprising the steps of mixing cenospheres separated from fly ash with a liquid binder containing phosphoric acid to produce a moldable paste; molding the paste into a mass having a desired physical configuration; and heating the molded mass to a temperature below that temperature at which sintering of the cenospheres occurs.

75

2. A method as claimed in claim 1 wherein the liquid binder further comprises a source of metal ions.

80

3. A method as claimed in claim 1 wherein the liquid binder is produced by adding to phosphoric acid a metal oxide, hydroxide or carbonate as a source of metal phosphate in the liquid binder, the molar ratio of metal phosphate to free phosphoric acid in the liquid binder being between 0.1/1 and 1/1.

85

4. A method as claimed in claim 1 wherein the liquid binder further comprises a source of metal ions, the liquid binder comprising a solution of metal phosphate in free phosphoric acid, the molar ratio of metal phosphate to free phosphoric acid in the liquid binder being between 0.1/1 and 1/1.

90

5. A method as claimed in claim 4 wherein the liquid binder is mixed with the cenospheres in a proportion by weight of one part liquid binder to 0.5 to 3.5 parts cenospheres.

95

6. A method as claimed in claim 1 wherein the molded mass further comprises an organic powder or beads of a material that volatizes during the heating step.

100

7. A method as claimed in claims 1 through 5 wherein the molded mass further comprises a material that foams during the heating step.

105

8. A method as claimed in claims 1 through 5 wherein the molded mass further includes fly ash as an inorganic filler.

110

9. A method as claimed in claims 1 through 8 wherein the temperature to which the molded mass is heated in the range of 200—950°C.

115

10. An inorganic composition that forms a rigid monolithic lightweight mass upon application of external heat; said composition comprising cenospheres separated from the fly ash formed when pulverized coal is burned, and phosphoric acid.

120

11. A composition as claimed in claim 10, further comprising a metal phosphate.

125

12. A composition as claimed in claim 10,

- further comprising a source of metal phosphate selected from materials reactive with phosphoric acid and containing aluminum, zinc, magnesium or chromium.
- 5 13. A composition as claimed in claim 10, further comprising a metal phosphate, the range of molar ratios of metallic phosphate to free phosphoric acid being 0.1/1 to 1/1.
- 10 14. A composition as claimed in claim 13 wherein the ratio by weight of metal phosphate and free phosphoric acid to cenospheres is in the range one part of metal phosphate and free phosphoric acid to 0.5 to 3.5 parts of cenospheres.
- 15 15. The product which results after heating a composition as claimed in any one of claims 10 to 14 to a temperature in the range of 200—950°C. for a period of 3 to 48 hours.
- 20 16. An inorganic composition that forms a rigid monolithic lightweight mass upon application of heat, said composition consisting essentially of a liquid binder comprising phosphoric acid, a source of metal ions and sufficient water to form a solution of metal phosphate and free phosphoric acid, and cenospheres separated from the fly ash formed when pulverized coal is burned.
- 25 17. A composition as claimed in claim 16 wherein the molar ratio of metal phosphate to free phosphoric acid is between 0.1/1 and 1/1.
18. A composition as claimed in claims 16 and 17 wherein the ratio by weight of liquid binder to cenospheres is in the range of one part of liquid binder to 3.5 parts of cenospheres.
19. The product which results after heating a composition as claimed in any one of claims 16 to 18 to a temperature in the range of 200—950°C. for a period of 3 to 48 hours.
20. A product as produced by the method claimed in any one of claims 1 to 9.
21. The method of producing the composition claimed in claims 10 through 19 and as described and set out herein.
22. A method of producing a lightweight composition as set forth in any of the foregoing Examples.
23. The composition produced by the method as claimed in claim 22.

WASHINGTON STATE UNIVERSITY
RESEARCH FOUNDATION, INC.,

Per: Boult, Wade & Tennant,
34, Cursitor Street,
London EC4A 1PQ.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.